

Supplementary Material

Effects of Ageing in Disinfectant Solution on the Corrosion Resistance and Antimicrobial Behavior of Copper Alloys

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The supplementary materials include four tables noted S1-S10

Table S1. Elementary composition (atomic %) of the different samples: Disinfectant on silicon substrate (D/Si), Copper, Former alloy and New alloy.

Sample/elementary composition	C at%	O at%	N at%	Cl at%	S at%	Na at%	Cu at%	Al* at%	Zn at%	Si at%
D/Si substrate	84.4	8.5	2.9	3	0.6	0.6	-	-	-	-
Copper 0h	32.4	27.4	1.45	1.35	-	-	37			
Copper 2h	54.6	26.7	3.7	0.9	3.1	-	11.1			
Copper 12h	69.5	12.4	8.6	1.4	4.4	-	4			
Copper 24h	63.8	18.7	6.9	1	3	-	7.6			
Copper 72h	71.2	11.1	9.15	1.35	4.65	-	2.65			
Former alloy 0h	34.5	32.2	1.1	0.45	-	-	19.65	11.25		
Former alloy 2h	55.7	22.5	7.65	1.55	2.05	-	7.55	3.65		
Former alloy 12h	67.55	9.65	12.85	2.5	4.5	-	3	-		
Former alloy 24h	68.1	13.3	9.9	1.8	3.4	-	3.5	-		
Former alloy 72h	72.15	9.45	10.1	1.6	4.55	-	2.2	-		
New alloy 0h	39.15	29.7	1.3	0.6	-		24.0		0.9	3.9
New alloy 2h	61	18.35	8.4	2	3.05		5.9		0.2	1.15
New alloy 12h	68.95	10.7	11.55	2.0	4.25		2.6		-	-
New alloy 24h	72.0	9.5	11.2	1.7	3.7		1.8		-	0.3
New alloy 72h	72.7	8.3	12.1	2.0	3.5		1.5		-	-

*NB: The at% of Al was calculated from the Cu_{3s} peak by subtracting the contribution of the Cu_{3s} peak. This contribution was estimated by the ratio of the Cu_{3s} / Cu_{2p3/2} area peaks with a pure copper.

Table S2. Proportion of chemical forms of carbon for: (a) Copper, (b) Former alloy and (c) New alloy, expressed as percentage of form relative to the total area of the peak.

Sample/Proportion of chemical forms	C-C / C-H	C-O / C-N	C=O/O-C-O	O-C=O
Copper 0h	53	29	12	6
Copper 2h	78	15	5	2
Copper 12h	75*	20*	4*	1*
Copper 24h	51	35	11	3
Copper 72h	86*	12*	1*	1*
Former 0h	63	23	9	5
Former 2h	66	22	8	4
Former 12h	60	24	14	2
Former 24h	71	23	5	1
Former 72h	88	11	-	1
New alloy 0h	62	26	9	3
New alloy 2h	75	18	4	3
New alloy 12h	63	22	13	2
New alloy 24h	49	37	12	2
New alloy 72h	54	23	18	5

Table S3. Proportion of chemical forms of copper on Copper, Former alloy and New alloy surface.

Samples/ chemical forms of copper	Cu 0	Cu I	Cu II	Satellite
Copper 0h	++	+	-	-
Copper 2h	-	++	++	++
Copper 12h	-	++	++	+
Copper 24h	-	+	+++	+
Copper 72h	-	+	+++	+
Former 0h	++	+	-	-
Former 2h	*	++	++	+
Former 12h	-	++	+++	+
Former 24h	-	+	+++	+++
Former 72h	-	+++	+	+
New alloy 0h	++	+	-	-
New alloy 2h	*	++	++	++
New alloy 12h	-	++	++	+
New alloy 24h	-	-	+++	+++
New alloy 72h	-	+++	++	+

* slight shoulder on the Auger peak which could correspond to the presence of a small proportion of metal shape.

Table S4. Proportion of nitrogen chemical forms for Copper, Former alloy and New alloy.

Sample/Nitrogen chemical forms	398 eV	399-400 eV	~ 402 eV
Copper 0h	31	69	-
Copper 2h	33	34	33
Copper 12h	35	40	26
Copper 24h	35	39	26
Copper 72h	33	39	28
Former 0h	48	43	8
Former 2h	49	44	7
Former 12h	34	47	19
Former 24h	36	45	19
Former 72h	33	40	27
New alloy 0h	31	51	18
New alloy 2h	39	48	13
New alloy 12h	37	48	15
New alloy 24h	30	48	22
New alloy 72h	34	45	21

Table S5. Proportion of chlorine chemical forms.

Sample/Chlorine chemical forms	Chlorine (198 eV)	Organic (200.5 eV)
D solution	100	-
Copper 0h	100	-
Copper 2h	64	36
Copper 12h	31	69
Copper 24h	31	69
Copper 72h	26	73
Former 0h	100	-
Former 2h	20	80
Former 12h	19	81
Former 24h	28	72
Former 72h	27	73
New 0h	100	-
New 2h	43	57
New 12h	17	83
New 24h	15	85
New 72h	15	85

Table S6. Proportion of sulfur chemical forms.

Samples name	Sulfide form (162 eV)	Sulfate and/or sulfonate forms (168-169 eV)
D solution	37	63
Copper 0h	-	-
Copper 2h	31	69
Copper 12h	42	58
Copper 24h	33	67
Copper 72h	39	61
Former 0h	-	-
Former 2h	43	57
Former 12h	44	56
Former 24h	29	71
Former 72h	39	61
New 0h	-	-
New 2h	40	60
New 12h	44	56
New 24h	39	61
New 72h	40	60

Table S7. Relative intensity of positive ions: cationic surfactant and unidentified species from D solution.

Sample	N° of tests	Intensity of substrate ⁶⁵ Cu (100%)	Cationic surfactant					Unidentified species from solution D				
			C ₁₂ H ₂₆ N	C ₁₆ H ₃₄ N	C ₁₈ H ₃₈ N	C ₂₂ H ₄₈ N	452 uma	466 uma	635 uma	1139 uma	1170 uma	1202 uma
Copper 0h	1 to 3	1 469 364	0.45	0.24	0.22	4.2	0.14	0.62	-	-	-	-
		1 449 800										
		1 507 234										
Copper 72h	1 to 3	154 036	803	259.3	206.6	2573.3	109.3	9	2.56	0.31	0.54	0.1
		89 813										
		111 941										
Former alloy 0h	1 to 3	575 605	1.13	0.79	0.553	6.53	-	-	-	-	-	-
		555 940										
		596 888										
Former alloy 72h	1 to 3	95 582	1330	389	298.3	3406.66	780	23.3	2.5	0.16	0.62	0.266
		87 247										
		103 441										
New alloy 0h	1 to 3	1 435 064	1.33	0.35	0.27	12.66	-	-	-	-	-	-
		1 374 332										
		1 301 584										
New alloy 72h	1 to 3	132 125	1370	420	332	2436.6	940.3	26.66	3.8	0.3	1.4	29.33
		124 237										
		123 896										

Table S8. Relative intensity of positive ions: metallic elements and Copper /oxygen compounds.

Sample	N° of tests	Intensity of substrate	Metallic elements					Copper/oxygen compounds			
			⁶⁵ Cu (100%)	Al	Ag*	Zn*	Si	Cu ₂ OH	⁶⁵ CuCu ₃ O	⁶⁵ CuCu ₄ O	⁶⁵ CuCu ₄ O ₂
Copper 0h	1 to 3	1 469 364	-	-	-	-	19.3	1.23	1.93	2.83	0.55
		1 449 800									
		1 507 234									
Copper 72h	1 to 3	154 036	-	-	-	-	22	-	-	-	-
		89 813									
		111 941									
Former alloy 0h	1 to 3	575 605	63.3	-	-	-	17	0.69	1.43	1.63	0.7
		555 940									
		596 888									
Former alloy 72h	1 to 3	95 582	0.74	-	-	-	10.26	-	-	-	-
		87 247									
		103 441									
New alloy 0h	1 à 3	1 435 064	-	-	-	5.36	21.6	1.13	2.03	2.53	0.55
		1 374 332									
		1 301 584									
New alloy 72h	1 à 3	132 125	-	-	-	1.16	11	-	-	-	-
		124 237									
		123 896									

*NB: Relative intensity of the positive ions corresponding to the Ag and Zn metallic elements has not identified by ToF- SIMS analyses. This shows that these elements has not found on the samples extreme surface.

Table S9. Relative intensity of positive ions: Aliphatic hydrocarbon species, Aromatic hydrocarbon species and Nitrogenous organic species.

Sample	N° of tests	Intensity of substrate	Aliphatic hydrocarbon compounds			Aromatic hydrocarbon compounds		Nitrogenous organic species		
		⁶⁵ Cu (100%)	C ₂ H ₅	C ₃ H ₇	C ₄ H ₉	C ₆ H ₅	C ₇ H ₇	CH ₄ N	C ₃ H ₈ N	C ₄ H ₁₀ N
Coppe 0h	1 to 3	1 469 364	57.6	66.33	20.66	5.96	4.4	4	193	2.6
		1 449 800								
		1 507 234								
Copper 72h	1 to 3	154 036	1560	2740	1343	112	72	105.3	3020	245.6
		89 813								
		111 941								
Former 0h	1 to 3	575 605	265.7	329.3	109.66	26.66	26.66	11.33	113	6.96
		555 940								
		596 888								
Former 72h	1 to 3	95 582	2180	3360	2006.66	87.66	87.66	163.33	3663.3	350.66
		87 247								
		103 441								
New 0h	1 to 3	1 435 064	103	120	49	10.6	9.5	5.13	25.33	3.033
		1 374 332								
		1 301 584								
New 72h	1 to 3	132 125	1950	2403.3	1543.33	129.33	81.66	144.66	2663.33	321.66
		124 237								
		123 896								

Table S10. Relative intensities (negative ions): sulfur and halogen species.

Sample	N° of tests	Intensity of substrate	Sulfur species								Nitrites/Nitrates		Halogen
		⁶³ Cu (100%)	S	HS	S ₂	CSN	SO ₂	SO ₃	SO ₄ H	S ₂ O ₈ H	NO ₂	NO ₃	Cl
Copper 0h	1 à 3	1 469 364	5	9.23	NM	2.5	52	315.33	60	NM	15.66	11.3	812.66
		1 449 800											
		1 507 234											
Copper 72h	1 à 3	154 036	1096.6	1763.33	77.33	280.33	2466.66	16200	13200	880	NM	NM	5990
		89 813											
		111 941											
Former alloy 0h	1 à 3	575 605	100.33	189	-	174.66	180.66	514.33	292.66	-	109.66	152.66	648.33
		555940											
		596888											
Former alloy 72h	1 à 3	95582	1493.33	2413.33	138.33	1024.66	3543.33	24633	9153.33	1533.33	114.33	376	21333.33
		87247											
		103441											
New alloy 0h	1 à 3	1 435 064	33.66	44.66	-	25.33	53	158	131.33	8.2	42.66	58.66	420.66
		1 374 332											
		1 301 584											
New alloy 72h	1 à 3	132 125	1136.66	1820	78.66	757.66	2633.33	17200	6380	1650	95.98	290.33	17000
		124 237											
		123 896											